

Synthesis and Characterization of Nano Crystalline MoO₃-TiO₂ Composite Thin Films by Liquid Phase Deposition Technique for Photodegradation Studies

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ABSTRACT: The composite compound films will have excellent color tone characteristics, glass characteristics, wear resistance and peel strength to be useful as decorative films on various substrates, visible light photochromic material for smart windows and display devices, as visible light photo catalysts for the degradation of organic dye in water, etc. Hence, to study photocatalytic properties of these materials, MoO₃-TiO₂ composite thin films were prepared at different composition by simple LPD technique on glass and Si substrate. The prepared films were annealed at different temperatures and characterized. The EDAX spectra support the existence of Ti, Mo, O atoms in mixed oxide films. XRD analysis shows the peaks corresponding to anatase phase of TiO₂ at 400°C with the orientation [010]. However, no peaks for MoO₃ were observed for the sample at lower percentage of MoO₃. This is due to highly dispersed or amorphous state MoO₃ on the surface of TiO₂. But at higher percentages of MoO₃, XRD lines appear with the orientation [021]. The intensity of this peak increases with increased in MoO₃ percentage. The SEM micrograph of MoO₃-TiO₂ thin film suggests the polycrystalline structure with the existence of MoO₃ and TiO₂ particles. The photo degradation result shows that the photocatalytic activity increases with increasing percentage of MoO₃ on TiO₂ surface. The sample composition, MoO₃ (20%)-TiO₂ (80%) and MoO₃ (40%)-TiO₂ (60%), exhibits photocatalytic activity more efficiently than bare TiO₂ thin film and the sample composition MoO₃ (60%)-TiO₂ (40%) under visible light.

Keywords - Composites, LPD Technique, MoO₃-TiO₂, Photo degradation, thin films

I. INTRODUCTION

In the past decade, a new field of materials chemistry has emerged that emphasizes the rational synthesis and study of nano crystalline materials. Much of this work is focused on semiconductor nanoparticles which display a variety of fundamentally interesting physical and chemical properties that are a direct result of their size and dimensionality. Many semiconductor compounds have potential for demonstrated technological importance in photoluminescence, solar energy conversion, photo catalysis etc., [1-25]. Cleaning contaminated air and industrial discharge is challenging issue for environmentalist. In these concerned, Civil Engineers play key role in capturing, treating and distributing water, and planning, developing and managing our water resources for the needs society. Providing facilities like treatment plants, pipelines, bridges, roads, canals, pump stations and dams etc. is as essential part of Civil Engineer. Even though biodegradation with microorganisms and chemical treatment with chlorine or ozone have been conventionally used for detoxification, their uses are limited due to adverse effect toxic compounds on microorganism, and by the need for large quantities of the oxidizing agent, respectively. For these reasons, the need for an alternative method for complete mineralization of various harmful organic compounds has been initiated. Several methods, such as “advanced oxidation processes”, have been employed by many researchers [26-27]. These methods commonly required high-energy source to produce hydroxyl radicals, which have an extremely high oxidation potential of ~ 2.0 eV [27] to induce chemical oxidation- reduction process. Among several advanced oxidation process, photo catalysis using UV light as an energy source with suspended powder or in the form of thin film has attracted the attention of many investigators due to its variety of applications. This photo catalysis has been applied even to wet solar cells, anti-fogging, and self-cleaning materials, as well as contaminated gas and water detoxification. The most frequently used semiconductor is TiO₂, because this satisfies the required conditions such as no toxicity, stability in aqueous solution, and no photo corrosion under bandgap illumination [12]. Titanium dioxide in the anatase form has bandgap energy of 3.2 eV and thus needs light below 388 nm to be capable of producing e⁻ and h⁺ pairs. Because light below 400 nm is only 4% of the solar energy reaching the surface of the earth, modified

photo catalysts have to be developed for solar applications. The novel photo catalysts must have efficiencies similar to, or more than, anatase-TiO₂ in absorbing the visible part of the solar spectrum. For this reason, it was initially thought that added dopant could exhibit red-shifted absorption spectra and also suppress recombination of charge carriers compared with pure TiO₂ [7,29-32]. In present studies, an effort has been made to synthesis nano-sized mixed oxides MoO₃- TiO₂ thin films with different Mo content by simple novel LPD technique. The influence of dopant in photo degradation properties has been studied.[33-36].

II. SYNTHESIS AND CHARACTERIZATION OF MOO₃- TiO₂

1. Experimental:

About 1.95g of 99.9% pure metallic Mo powder (Fluka Chem.) was slowly dissolved in ice-cold solution of 30% H₂O₂ and acetic acid. The reaction mixture was kept overnight at a temperature ranging from 0-12°C. The solution was then filtered and mixed with 0.5 % aqueous solution of NH₄F·HF (ammonium bifluoride).

On the other hand TiO₂ precursor is prepared by dissolving ammonium hexa- fluorotitanate and boric acid in distilled water so that the concentration of Ti ion is about 0.15 mol./ dm³ and boric acid concentration is about 0.05 mol. /dm³. Various amounts of above two solutions were combined to afford mixture with different MoO₃/TiO₂ ratios. (20:80, 40:60, 60: 40). The glass and Si (100) substrate after degrease and cleaned ultrasonically, is placed vertically in a precursor. The experimental solution is kept at 30°C for about 20-40 hours. They were then removed and washed with doubled distilled water. The films thus obtained are annealed at different temperatures.

2. Result and discussion:

Structure and morphology:

EDAX analysis: The elemental analysis of the mixed oxides thin film was ascertained by taking EDAX spectra. The existence of peaks corresponding to Mo, Ti and oxygen confirms the formation of MoO₃TiO₃ mixed oxide films (Fig.a).

X-ray powder diffraction (XRPD) studies are carried out to ascertain the crystallographic structures of the MoO₃- (TiO₂) x thin films. The XRD pattern of MoO₃ (20%)- TiO₂(80%) thin films annealed at 400°C shows an anatase TiO₂ phase (Fig.b:1) with (010) orientation but the peaks corresponding MoO₃ were not found. The absence of XRD peaks at lower concentration of MoO₃ is due to highly dispersed or amorphous state MoO₃ on the surface of TiO₂. However the XRD lines with d value 3.2211, 3.1249, and 2.1821 Å appeared due to crystalline MoO₃ phase at higher percentage of MoO₃ (Fig b:2). The most intense XRD line due to MoO₃, corresponding to the (021) plane at d value 3.129Å, was observed only at 40% MoO₃ in the sample annealed at 400°C. The intensity of this peak increases with increase of MoO₃ percentage.

The SEM micrograph of MoO₃-TiO₂ thin films at different compositions is shown in Fig.c:1- c:3. The Fig.c:1 shows the microstructure of MoO₃ (20%) – TiO₂ (80%) thin films on Si (100) substrate at 400°C. The SEM image suggested the polycrystalline structure with the existence of MoO₃ and TiO₂ particles. This is also confirmed by EDAX data. Large particles of MoO₃ readily exist in the film of composition MoO₃ (40%) – TiO₂ (60%) and MoO₃ (60%) - TiO₂ (40%) sample (Fig c:2- c:3).

Photo degradation properties: MoO₃- TiO₂ thin film is placed in aqueous solution of methyl orange taken in glass beaker. The concentration of methyl orange is about 10 ppm. The solution was exposed to sun light for different irradiation time (10-40min.). The solution was bubbled frequently with air during irradiation and then scanned by UV- Visible spectrophotometer after every 10 min at the wave length range from 300-1000nm to measure the absorbance.

The degradation result shows the photocatalytic activity increases with increasing the percentage of MoO₃ on TiO₂ surface. The sample composition MoO₃ (20%) - TiO₂ (80%) and MoO₃ (40%) - TiO₂ (60%) exhibits photocatalytic activity much efficiently than the bare TiO₂ thin films and the sample composition MoO₃ (60%)- TiO₂(40%) under visible light. It was found that methyl orange dye undergoes decolourisation effectively in

presence MoO₃ (20%)- TiO₂(80%) and MoO₃(40%)- TiO₂(60%).But poor result was observed for the sample MoO₃ (60%)- iO₂(40%).(Fig's) It is well known fact that, in mixed oxide photo catalyst the transfers of photo excited electrons from TiO₂ to MoO₃ result in formation of Mo⁵⁺. This trapping of electron by Mo⁶⁺ favorably increases the life time of hole and hence photo degradation is effective [33-35]. It was observed that as the concentration of MoO₃ increases, the trapping of electrons also increases, however at higher concentration of MoO₃ (60:40), the rate of recombination of e⁻ - h⁺ pair starts dominating, hence photocatalytic activity decreases [36]. The recombination of e⁻ - h⁺ pair can be explained by the following reactions.



III. RESULTS

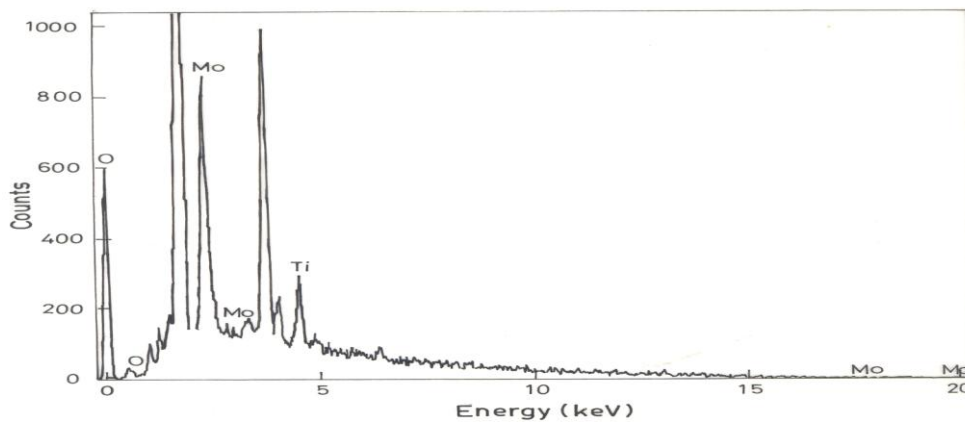


Fig.1: EDAX spectra of MoO₃ – TiO₂ composite film

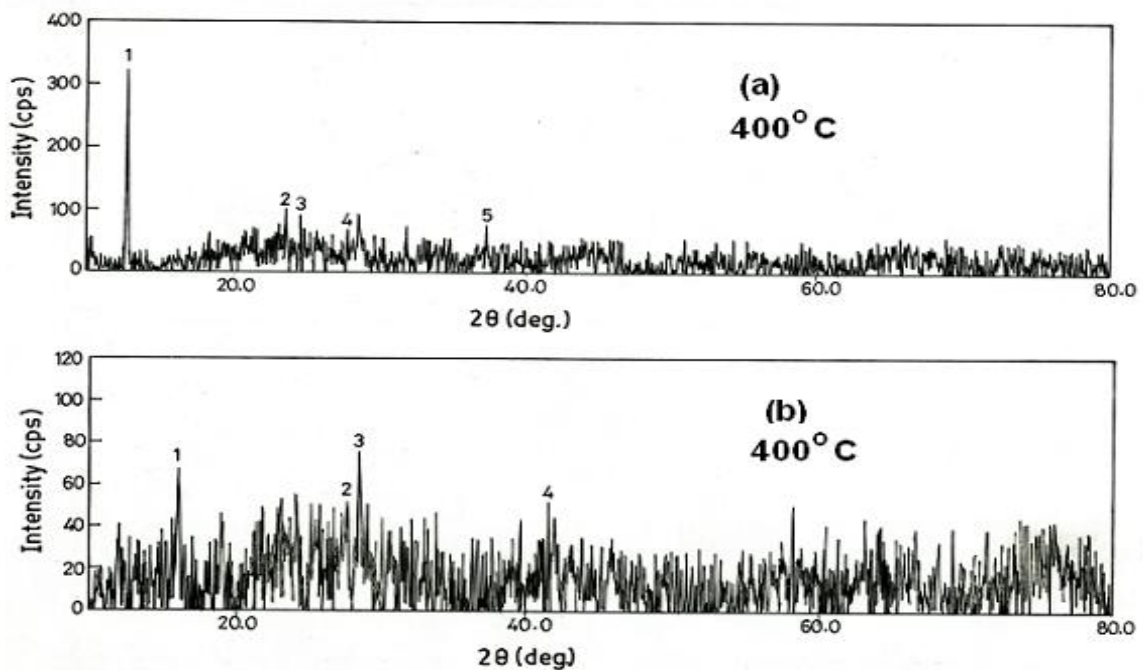


Fig.2: XRD Pattern Of MoO₃. TiO₂ Thin Films At Different Concentration Of MoO₃; B:1) MoO₃ (20%) - TiO₂ (80%), Annealed At 400°c, B: 2) MoO₃ (40%)- TiO₂(60%), Annealed At 400°c

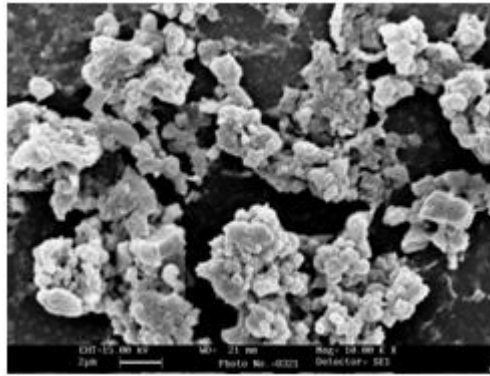


Fig.3: SEM of MoO₃-TiO₂ (20:80) Thin Film Annealed At 400°C

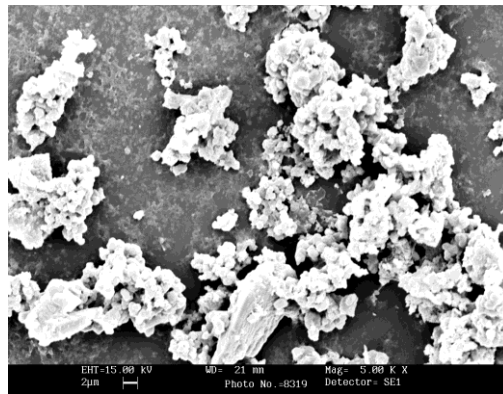


Fig.4: SEM of MoO₃- TiO₂ (40: 60) thin film annealed at 400°C.

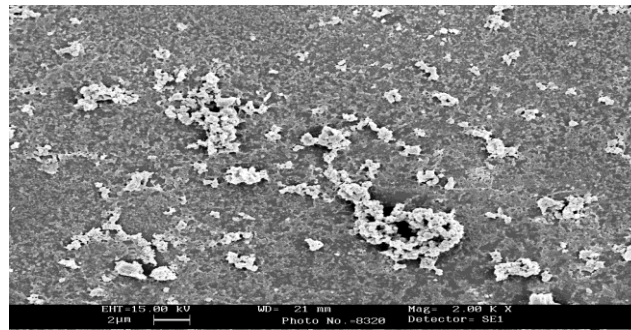


Fig. 5: SEM of MoO₃- TiO₂ (60:40) Thin Film Annealed At 400°C

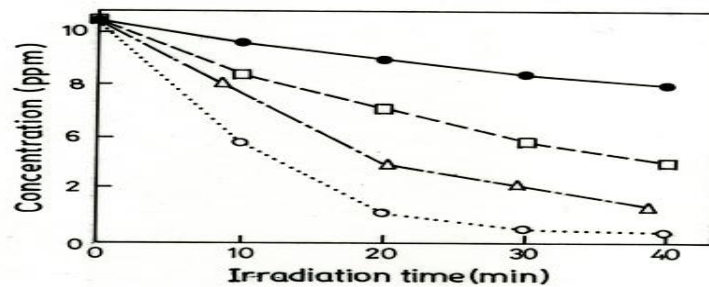


Fig.6: Photocatalytic Degradation of Methyl Orange Indicator at Different Irradiation Time: A) Degradation By MoO₃- TiO₂ (40:60) Thin Films B) MoO₃- TiO₂ (20:80) D) MoO₃- TiO₂ (60:40) C) Bare TiO₂ Thin Films

III. CONCLUSION

The composite photo catalyst MoO₃-TiO₂, were developed on glass and Si substrate by a simple novel technique known as LPD technique in order to study photo degradation of methyl orange dye in water. The composition of the films was ascertained by recording EDAX spectra, XRD analysis shows the peaks corresponding to anatase phase of TiO₂, at 400°C with the orientation [010]. But no peaks for MoO₃ was observed for the sample composition MoO₃ (20%) – TiO₂ (80%). This is due to higher percentage of MoO₃, XRD lines were appeared with the orientation [021]. The intensity of this peak increases with increase of MoO₃ percentages.

The photo degradation result shows the photocatalytic activity increases with increasing the percentage of MoO₃ on TiO₂ surface. But at higher concentration of MoO₃ (60:40), the rate of recombination of e⁻ - h⁺ pair starts dominating and hence photocatalytic activity decreases.

The results of the present investigation on simple transition metal oxide composite thin films grown by LPD technique is observed to give a very wide scope for Environmental Engineering to remove color from the waste water, de-colorization of effluent from textile dyeing and finishing industry was regarded important because of aesthetic and environmental concerns. The photo catalyst in the form of nano thin films has its own advantages when compare to bulk catalyst because the catalyst can be reused for several time and degradation take place under visible light.

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